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(54) COMPOSITION FOR LIQUID CRYSTAL ALIGNMENT FILM, LIQUID CRYSTAL ALIGNMENT FILM, LIQUID CRYSTAL HOLDING SUBSTRATE AND LIQUID CRYSTAL DISPLAY DEVICE

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a polyimide oriented film without causing defective orientation due to mechanical or thermal stress by using a specified amt. of an arom. diamine having a methylene group on the principal chain.
SOLUTION: At the time of producing a compsn. for a liq. crystal alignment film contg. polyamic acid obtd. by allowing an arom. diamine to react with tetracarboxylic acid anhydride, an arom. diamine having a methylene group on the principal chain is used by 10-55mol% of the arom. diamine. A bendable structure is introduced into the structure of the principal chain of polyimide and mechanical or thermal stress applied to a film to be oriented by treatment after film formation, especially by rubbing is easily relieved. The film is efficiently oriented and liq. crystal orienting property is improved. The pref. amt. of the arom. diamine having a methylene group on the principal chain is 10-50mol%, especially 10-30mol%.

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CLAIMS

[Claim(s)]
[Claim 1] The constituent for liquid crystal orientation film characterized by being the aromatic series diamine to which inner 10-55-mol% of aromatic series diamine has a methylene group on a principal chain in the constituent for liquid crystal orientation film containing the polyamide acid which aromatic series diamine and a tetracarboxylic acid anhydride are made to react, and is obtained.
[Claim 2] Liquid crystal orientation film obtained by applying, drying and carrying out the dehydration ring closure of the constituent for liquid crystal orientation film according to claim 1 to a substrate, forming a polyimide layer and subsequently carrying out rubbing of this polyimide layer.
[Claim 3] The liquid crystal pinching substrate which comes to form the liquid crystal orientation film according to claim 2 on the field in which the electrode was formed.
[Claim 4] The liquid crystal display component which comes to pinch liquid crystal between liquid crystal pinching substrates according to claim 3.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the constituent for liquid crystal orientation film, the liquid crystal orientation film, a liquid crystal pinching substrate, and a liquid crystal display component.
[0002]
[Description of the Prior Art] The aromatic polyimide (refer to JP,55-10180,B) which is made to carry out the condensation reaction of 4 and 4'-diamino diphenyl ether and the pyromellitic acid 2 anhydride, and is obtained as orientation film for liquid crystal display components is conventionally made into the start. Recently, from the demand of the transparency of a display device, or the high pre tilt angle of liquid crystal The polyimide which is made to carry out the condensation reaction of the diamine which has a perfluoroalkyl radical, the tetracarboxylic acid which has alicyclic structure, or its derivative, and is obtained (refer to JP,63-259515,A), The aromatic polyimide (refer to JP,64-25126,A) which is made to carry out the condensation reaction of 2 and 2-screw [4-(4-amino phenoxy) phenyl] octane and the pyromellitic acid 2 anhydride, and is obtained is proposed.
[0003]
[Problem(s) to be Solved by the Invention] Thus, in spite of having made various devices, poor orientation might be produced by processing, and the mechanical stress and thermal stress after film formation which are especially added by rubbing processing. This invention aims at offering the constituent for obtaining the polyimide orientation film which produces poor orientation neither by mechanical stress nor thermal stress, and this orientation film.
[0004]
[Means for Solving the Problem] This invention is a constituent for liquid crystal orientation film characterized by being the aromatic series diamine to which inner 10-55-mol% of aromatic series diamine has a methylene group on a principal chain in the constituent for liquid crystal orientation film containing the polyamide acid which aromatic series diamine and a tetracarboxylic acid anhydride are made to react, and is obtained.
[0005] This constituent for liquid crystal orientation film is used, it applies and dries and a dehydration ring closure is carried out to a substrate, and a polyimide layer is formed, subsequently rubbing of this polyimide layer is carried out, and it considers as the liquid crystal orientation film. Moreover, the liquid crystal orientation film is formed on the field in which the electrode was formed, and it considers as a liquid crystal pinching substrate, and between two liquid crystal pinching substrates, liquid crystal is pinched and it considers as a liquid crystal display component.
[0006] It is alike rattlingly, turnable structure is introduced more in the polymer principal chain structure of polyimide, and inner 10-55-mol% of aromatic series diamine becomes easy to ease the mechanical and thermal stress which is the aromatic series diamine which has a methylene group on a principal chain and which joins the orientation film by processing, especially rubbing processing, etc. after orientation film formation. Therefore, orientation processing is carried out efficiently and the orientation film is considered that effectiveness is in the improvement in a stacking tendency.
[0007] the mol of the aromatic series diamine which has a methylene group on a principal chain in order to make stress easy to introduce turnable structure in polymer principal chain structure, and to ease -- more than 10 mol % of the diamine by which a number is used for a reaction -- it is required. On the other hand, since introducing a methylene group on a principal chain reduces the glass transition point of polyimide and it degrades thermal stability, the number of mols of the aromatic series diamine which has a methylene group on a principal chain is made into less than [of the diamine used for a reaction / 55 mol %]. In addition, it is desirable that the aromatic series diamine which has a methylene group on a principal chain considers as 10-50-mol % from relaxation of stress and a viewpoint of the balance of thermal stability, and it is most desirable to consider as 10-30-mol %.
[0008]
[Embodiment of the Invention] As the methylene group on a principal chain shows ** 1, when continuing, it is desirable that it is 16 or less, as for n, it is more desirable that it is 14 or less, and it is most desirable that it is 12 or less. The thermal resistance of the polyimide which will be obtained if n is large worsens.
[Formula 1] - CH2n - as such aromatic series diamine - diamino diphenylmethane, and 4 and 4 '3, 4'-diamino diphenylmethane, 3 and 3' screw [- diamino diphenylmethane, 1, and 2-] [4-amino phenoxy] ethane, 1 and 3-screw [4-amino phenoxy] propane, 1, 4-screw [4-amino phenoxy] butane, 1 and 5-screw [4-amino phenoxy] pentane, the JI [2-(4-amino phenoxy) ethyl] ether, 1 and 2-screw [2-(4-amino phenoxy) ethoxy] ethane, the JI (2-(2-[4-amino phenoxy] ethoxy) ethyl) ether, 1 and 2-screw [4-aminophenyl] ethane, JI (4-diamino -3 methylphenyl) methane, JI (4-diamino -3, 5-dimethylphenyl) methane, JI (4-diamino-3-ethyl-5-methylphenyl) methane, JI (4-diamino -3, 5-diethyl phenyl) methane, etc. are mentioned, and these can also use two or more sorts together.
[0009] Moreover, there is especially no limit about diamines other than the aromatic series diamine which has a methylene group on the above-mentioned principal chain. 4 and 4'-diamino diphenyl ether, 1, 4-diaminobenzene, 1, 4-diamino - 2, 3, 5, 6-tetramethyl benzene, 2, and 2-screw (4-(4-amino phenoxy) phenyl) propane, 2 and 2-screw (4-(4-amino phenoxy) phenyl) - 1, 1, 1, 3, 3, and 3-hexafluoropropane, 1, and 8-diamino octane etc. is mentioned, and these can also use two or more sorts together.
[0010] As diamine and tetracarboxylic dianhydride made to react Pyromellitic acid 2 anhydride, methyl pyromellitic acid 2 anhydride, dimethyl pyromellitic acid 2 anhydride, JI (trifluoromethyl) pyromellitic acid 2 anhydride, 3, 3', 4, 4'-biphenyl tetracarboxylic dianhydride,

- dimethyl -3, 3', and 5 and 5 '4, 4'-biphenyl tetracarboxylic dianhydride, p-(3, 4-dicarboxy phenyl) benzene 2 anhydride, 3, 3', 4, and 4' - tetra-carboxy diphenyl ether -- 2 anhydride 2, 3, 3', and 4' - tetra-carboxy diphenyl ether -- 2 anhydride 3, 3', 4, and 4' - tetra-carboxy benzophenone 2 anhydride, 1, 4 and 5, and 7-tetra-carboxy naphthalene -- 2 anhydride 1, 2, 5, 6-tetra-carboxy naphthalene 2 anhydride, 3, 3', 4, and 4' - tetra-carboxy diphenylmethane -- 2 anhydride 2 and 2-screw (3, 4-dicarboxy phenyl) propane 2 anhydride, 2 and 2-screw (3, 4-dicarboxy phenyl) - 1, 1, 1, 3, 3, and 3-hexafluoropropane 2 anhydride, 3, 3', 4, and 4' - tetra-carboxy diphenylsulfone -- 2 anhydride 3, 4, 9, 10-tetra-carboxy perylene 2 anhydride, 3, 3', 4, 4'-ethylene glycol screw (phenyl) tetracarboxylic dianhydride, 1, 2, 4, 5-cyclohexane tetracarboxylic dianhydride, 1, 2 and 3, 4-cyclobutane tetracarboxylic dianhydride, 1, 2 and 3, 4-butane tetracarboxylic dianhydride, etc. are mentioned, and these can also use two or more sorts together.

[0011] The aromatic series diamine which has a methylene group on a principal chain, diamines other than the aromatic series diamine which has a methylene group on a principal chain, and tetracarboxylic dianhydride are made to dissolve and react to an inert solvent, and it considers as a polyamide acid.

[0012] As for total of the number of mols of the aromatic series diamine which has a methylene group on a principal chain, and the number of mols of diamines other than the aromatic series diamine which has a methylene group on a principal chain, and total of the number of mols of tetracarboxylic dianhydride, at this time, it is desirable to make it equimolar mostly and to make it react.

[0013] As an inert solvent, although it is not necessary to dissolve said all monomers, what dissolves the polyamide acid to generate is desirable, for example, one sort, such as a N-methyl-2-pyrrolidone, N.N-dimethylformamide, N,N-dimethylacetamide, dimethyl sulfoxide, a tetramethyl sulfone, and 1,4-dioxane, or two sorts or more are used. In addition to these solvents, the solvent for [to a glass substrate] being smeared and improving a sex can also be added before a reaction or after reaction termination. Butyl cellosolve, butyl-cellosolve acetate, a xylene, toluene, etc. are used as these solvents.

[0014] Let the polyamide acid obtained at the reaction be polyimide by carrying out a chemical treatment with dehydrating agents, such as heating at 100-400 degrees C, and/or an acetic anhydride. An electrode is prepared in the side which faces the liquid crystal on a liquid crystal pinching substrate, the liquid crystal orientation film obtained from a liquid crystal orientation film constituent on this substrate and an electrode is formed, and it considers as a liquid crystal display component.

[0015] After the formation on the liquid crystal substrate of the polyimide layer of this invention applies the solution of the polyamide acid generated at the above-mentioned reaction on the glass substrate with which transparent electrodes, such as ITO (Indium Tin Oxide), were formed beforehand, for example, it dries and it is performed by carrying out a dehydration ring closure and considering as a polyimide layer. As the method of application, dip coating, print processes, a blasting method, etc. are used. 100-400 degrees C of dehydration ring closure temperature can be preferably chosen as arbitration in 150-300 degrees C. Moreover, heating time is preferably made into 1 minute - 3 hours for 1 minute to 6 hours.

[0016] Thus, the formed polyimide layer is used as liquid crystal orientation film by carrying out rubbing of the front face. A liquid crystal display component can be obtained by the well-known approach using the liquid crystal display substrate which has the liquid crystal orientation film.

[0017]

[Example] Hereafter, an example explains this invention.

[0018] An example 14, the 4'-diamino diphenylmethanes 4.0g (0.02 mols) and 1, 4-diamino - After adding 221g of N-methyl-2-pyrrolidones to 2, 3, 5, and 6-tetramethyl benzene 13.1g (0.08 mols) and agitating enough, when it added 21.8g (0.10 mols) of pyromellitic acid 2 anhydrides and was made to react at 20 degrees C for 8 hours, it became a liquid with viscous light yellow. It applied on the glass substrate with which the ITO transparent electrode was formed so that viscosity control of this solution might be carried out and it might become 640x200 dots, and it heated at 250 degrees C for 30 minutes, removal of a solvent and the dehydration ring closure of a polyamide acid were performed, and the polyimide layer with a thickness of 60nm was formed. Next, rubbing processing of this polyimide layer front face was carried out, and the liquid crystal pinching substrate was obtained. As the direction of rubbing became antiparallel, as the polyimide layer countered, it combined these two liquid crystal pinching substrates, the surroundings were closed by the epoxy system sealing compound (trade name EN-1000 by Hitachi Chemical Co., Ltd. were used), and the cel was assembled. When liquid crystal (trade name ZLI-2293 by Merck Co. were used) was enclosed in the assembled cel, the liquid crystal cell was formed and the pre tilt angle was measured, the pre tilt angle was 3.1 degrees. Moreover, as it became 90-degree twist about said two liquid crystal pinching substrates, the liquid crystal (trade name ZLI-2293 by Merck Co.) which added the chiral agent (trade name CB-15 by Merck Co. were used) was enclosed in the cel which assembled and assembled the cel like the following. This obtained liquid crystal display component showed good orientation.

[0019] Example 2 JI (4-diamino-3-ethyl-5-methylphenyl) methane 14.1g (0.05 mols) and 1, 4-diamino - After adding 324g of N-methyl-2-pyrrolidones to 2, 3, 5, and 6-tetramethyl benzene 8.2g (0.05 mols) and agitating enough, when it added 21.8g (0.10 mols) of pyromellitic acid 2 anhydrides and was made to react at 25 degrees C for 12 hours, it became a liquid with viscous light yellow. It was 4.3 degrees, when made temperature of removal of a solvent, and the dehydration ring closure of a polyamide acid into 270 degrees C, and time amount was made into 1 hour using this solution, and also the liquid crystal cell was obtained like the example 1 and the pre tilt angle was measured. Moreover, the liquid crystal display component of 90-degree twist was formed by the same approach. This liquid crystal display component showed good orientation.

[0020] An example 34, the 4'-diamino diphenylmethanes 6.0g (0.03 mols) and 2, 2-screw (4-(4-amino phenoxy) phenyl) - 316g of N-methyl-2-pyrrolidones is added to 1, 1, 1, 3, 3, and 3-hexafluoropropane 36.3g (0.07 mols). pyromellitic acid after agitating enough 2 anhydrides 10.9g (0.05 mols) and 3, 3', 4, and 4' -- when 16.1g (0.05 mols) of - tetra-carboxy benzophenone 2 anhydrides was added and it was made to react at 30 degrees C for 5 hours, it became a liquid with viscous light yellow. It was 4.3 degrees, when the liquid crystal cell was obtained like the example 2 using this solution and the pre tilt angle was measured. Moreover, the liquid crystal display component of 90-degree twist was formed by the same approach. This liquid crystal display component showed good orientation.

[0021] The example 11 of a comparison, 4-diamino - After adding 217g of N-methyl-2-pyrrolidones to 2, 3, 5, and 6-tetramethyl benzene 16.4g (0.10 mols) and agitating enough, when it added 21.8g (0.10 mols) of pyromellitic acid 2 anhydrides and was made to react at 20 degrees C for 8 hours, it became a liquid with viscous light yellow. When the liquid crystal display component was created like the example 2 using this solution, poor orientation occurred.

[0022] Example of comparison 2 JI (4-diamino-3-ethyl-5-methylphenyl) methane 16.9g (0.06 mols) and 1, 4-diamino - After adding 332g of N-methyl-2-pyrrolidones to 2, 3, 5, and 6-tetramethyl benzene 6.6g (0.04 mols) and agitating enough, when it added 21.8g (0.10 mols) of pyromellitic acid 2 anhydrides and was made to react at 25 degrees C for 12 hours, it became a liquid with viscous light yellow. When

the liquid crystal display component was created like the example 2 using this solution, poor orientation occurred.
[0023] The example 32 of a comparison, 2-screw (4-(4-amino phenoxy) phenyl) - 359g of N-methyl-2-pyrrolidones is added to 1, 1, 1, 3, 3, and 3-hexafluoropropane 51.9g (0.10 mols). pyromellitic acid after agitating enough 2 anhydrides 10.9g (0.05 mols) and 3, 3', 4, and 4' -- when 16.1g (0.05 mols) of - tetra-carboxy benzophenone 2 anhydrides was added and it was made to react at 30 degrees C for 5 hours, it became a liquid with viscous light yellow. When the liquid crystal display component was created like the example 2 using this solution, poor orientation occurred.
[0024]
[Effect of the Invention] The liquid crystal orientation film is formed with the constituent for liquid crystal orientation film of this invention, when a liquid crystal display component is created using the liquid crystal display substrate which has this liquid crystal orientation film, a stacking tendency becomes good and the liquid crystal display component of good display quality can be obtained.

[Translation done.]